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Dissolution of metal oxides in an acid-saturated ionic liquid solution and investigation of the back-extraction behaviour to the aqueous phase

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Abstract

The dissolution of metal oxides in an acid-saturated ionic liquid, followed by selective stripping of the dissolved metal ions to an aqueous phase is proposed as a new ionometallurgical approach for the processing of metals in ionic liquids. The hydrophobic ionic liquid trihexyl(tetradecyl)phosphonium chloride (Cyphos IL 101) saturated with a concentrated aqueous hydrochloric acid solution was used to dissolve CaO, NiO, MnO, CoO, CuO, ZnO and Fe_2O_3. It was found that nickel(II) and calcium(II) could be separated from all other transition metals present in the ionic liquid phase by stripping at high chloride concentrations. By scrubbing the ionic liquid solutions phase with water, manganese(II) and cobalt(II) could be stripped together with a fraction of iron(III) and copper(II), leaving zinc(II) and the remainder of copper(II) and iron(III) in the ionic liquid phase. These metal ions could be removed from the ionic liquid using ammonia. Copper(II) and zinc(II) formed ammine complexes and were back-extracted, while iron(III) precipitated as iron(III) hydroxide. After removal of all the metals present in the ionic liquid phase, the ionic liquid was prepared for reuse. Unfortunately, the mutual separations nickel–calcium, cobalt–manganese, or zinc–copper could not be achieved. This system would be useful when nickel is the metal of interest, since separation of nickel from all other transition metals present in the solution is achieved by one stripping step.

Key Words: Ionic liquids – leaching – metal oxide dissolution – selective stripping - trihexyl(tetradecyl)phosphonium chloride

Introduction

Ionic liquids (ILs) are a relatively new class of solvents which are entirely made of ions and possess a melting point below 100 °C (Welton, 1999). Other characteristic properties include a high electrical conductivity, a large electrochemical window, a broad liquidus range, and a high thermal stability (Anthony et al., 2003). These properties make ionic liquids perfectly suitable solvents for a broad range of application fields such as catalytic and chemical reactions (Plechkova and Seddon, 2008; Wasserscheid and Keim, 2000), membrane technology (Bara et al., 2010; Cserjesi and Belafi-Bako, 2011; Han and Row, 2010), separation technology (Han and Row, 2010), nanotechnology (Antonietti et al., 2004; Deshmukh et al., 2001; Fonseca et al., 2004), and analytical chemistry (Koel, 2005; Soukup-Hein et al., 2009). Solvent extraction (SX) is a technique often used to separate metal ions from each other (Rydberg et al., 1992), and there have been a number of reports of the utilisation of ionic liquids (Billard et al., 2011; Dai et al., 1999; Dietz, 2006; Stojanovic and Keppler, 2012; Visser et al., 2001). Trihexyl(tetradecyl)phosphonium chloride, the ionic liquid used in this study, has been shown to be an environmentally friendly extraction phase for metal ions when applied in undiluted form (Vander Hoogerstraete et al., 2013; Wellens et al., 2012). In addition, ionic liquids can be used as solvents for the electrochemical recovery of metals (Abbott et al., 2011a; Abbott et al., 2011b). For electrowinning, ionic liquids should have a high solubilising power for metal salts, including metal oxides. However, the solubility of metal oxides in ionic liquids is in general very low, this is because no oxide-binding reagent able to react with the metal oxide is present and because of the high strength of many metal-oxide bonds. Nevertheless, some examples of ionic liquids that were able to dissolve metal oxides have been reported (Abbott et al., 2011b; Tian et al., 2010).

Dai et al. and later Bell et al. reported the solubility of uranium(VI) oxide and vanadium (V) oxide, respectively, in imidazolium chlororoaluminate ionic liquids (Bell et al., 1999; Dai et

al., 1997). Unfortunately, chloroaluminate ionic liquids are not suitable for ionometallurgical processing of metal oxides, since these ionic liquids are extremely sensitive to moisture. Abbott and co-workers were able to dissolve a range of metal oxides in deep-eutectic solvents (DES), which are mixtures of choline chloride with a hydrogen-bond donor and are solvents with properties similar to those of ionic liquids (Abbott et al., 2006a; Abbott et al., 2006b; Abbott et al., 2005; Abbott et al., 2003). Nockemann et al. used protonated betaine bis(trifluoromethylsulfonyl)imide and similar ionic liquids for the dissolution of several metal oxides including the rare-earth oxides, uranium(VI) oxide, zinc(II) oxide, copper(II) oxide and nickel(II) oxide (Nockemann et al., 2006; Nockemann et al., 2008). These examples of ionic liquids were able to react with the oxides because of the presence of reactive protons in the cationic core of the ionic liquid. The availability of reactive protons is essential for the dissolution of metal oxides in ionic liquids. However, conventional protic ionic liquids cannot be used for this dissolution process, because upon reaction with the metal oxide, the ionic liquid is transformed into a neutral amine base. Moreover, many protic ionic liquids contain substantial amounts of neutral entities, unless they are prepared by very strong Brønsted acids (Greaves and Drummond, 2008). Ionic liquids with acid anions such as hydrogen sulphate have been used for the leaching of metals from ores. Unfortunately, the number of possible anions is limited to partially deprotonated polyprotic acids (Dong et al., 2009; Whitehead et al., 2004; Whitehead et al., 2007; Whitehead et al., 2009). Furthermore, hydrogen sulphate ionic liquids were used for the dissolution of alumina for electrolysis applications (Ma et al., 2007; Tian et al., 2010).

In this paper, we propose another approach to the dissolution of metal oxides in ionic liquids, namely by using an acid-saturated ionic liquid solution. More in particular, the dissolution of CaO, NiO, MnO, CoO, CuO, ZnO and Fe_2O_3 in the ionic liquid trihexyl(tetradecyl)phosphonium chloride (Cyphos® IL 101) saturated with hydrochloric acid

has been investigated. The stripping of the dissolved metals from the ionic liquid phase to an aqueous phase is described and the selective removal of metals from the ionic liquid offers possibilities for the separation of mixtures of metal ions especially for nickel. Finally, the regeneration of the ionic liquid is considered.

Experimental

Chemicals

Trihexyl(tetradecyl)phosphonium chloride $P_{66614}Cl$ (>97%; Cyphos® IL101; Cytec Industries), HCl (37%, VWR), 1,4-dioxane (>99%; extra pure; stabilised, Acros Organics), ammonia (25 wt%, Chem-Lab NV), Fe_2O_3 (purified, Sigma-Aldrich), CaO (pieces made from marble, RPR), MnO (powder; 60 mesh; 99%, Sigma-Aldrich), NiO (76% Ni, Acros Organics), CoO (95%; powder, Alfa Aesar), CuO (≥99%, Sigma-Aldrich) and ZnO (≥99%, Sigma-Aldrich) were used as received, i.e. without further purification.

Instrumentation and methods

The metal content of the ionic liquid phases and aqueous phases was determined using a benchtop total reflection X-ray fluorescence (TXRF) spectrometer (Picofox S2, Bruker). For analysis of the aqueous phase by TXRF, aqueous samples (1 mL) were measured after addition of gallium as an internal standard. The samples were diluted with MilliQ water (if necessary). A small aliquot of 10 µL was applied on a quartz glass carrier, dried by evaporation in a hot air oven (60 °C) and measured with a measurement time of 200 s. For the determination of the metal content in an organic phase by TXRF, a certain weight of the extracted phase (± 0.5 g) was diluted in dioxane (20 mL). Gallium (1000 mgL^{-1}, in HNO_3 2-3 %) was added to the solution as an internal standard. A small aliquot of 5 µL was applied on a quartz glass carrier, dried by evaporation in a hot air oven (60 °C) and measured with a

measurement time of 400 s. Absorption spectra were measured with a Varian Cary 5000 spectrophotometer. A quartz cuvette with an optical path length of 0.1 mm was used. ^{31}P NMR spectra were recorded on a Bruker Avance 400 spectrometer, operating at 161.98 MHz for ^{31}P. The samples were measured in a NMR tube containing a sealed capillary with deuterated chloroform (an external lock). A delay time (d1) of 60 s was applied in the NMR pulse sequence to avoid saturation effects in the ^{31}P NMR.

Dissolution experiments

10 wt% hydrochloric acid (12 M HCl) was dissolved in the ionic liquid trihexyl(tetradecyl)phosphonium chloride (50 mL). To this solution, NiO, CuO, Fe_2O_3, ZnO, CaO, MnO and CoO were added with a metal concentration of 1 g L^{-1} for each metal. The ionic liquid solutions were analysed for their metal content after intensively stirring for two hours at 60 °C.

Stripping experiments

To carry out the stripping experiments, a sample (4 mL) of the $P_{66614}Cl$–HCl phase containing the dissolved metal ions was taken and mixed with an aqueous solution (4 mL). This aqueous solution contained HCl concentrations ranging from 0 M (pure water) to 12 M. The solutions were stirred for 30 minutes at 60 °C. After phase separation, the phases were centrifuged (3000 rpm, 3 min) and both phases were analysed for their metal content.

The recovery of the ionic liquid was tested after stripping of copper, zinc and iron. To three individual batches of the $P_{66614}Cl$ –HCl solution (5 mL), Fe_2O_3 and CuO and ZnO were added, respectively, so that after dissolution the ionic liquid phase had a metal content of 5 g L^{-1}. After the dissolution of the metal oxides, the ionic liquid solution was washed twice with

water (5 mL). Thereafter, the ionic liquid phase was mixed with an aqueous ammonia solution (5 wt% NH_3, 5 mL). After centrifugation the ionic liquid phases were analysed for their metal content. After the stripping step at 6 M HCl, the ionic liquid phase (4 mL), was subsequently mixed three times with a pure water solution (4 mL). Finally, an ammonia solution (5 wt%) was used as stripping solution (4 mL). The stripping conditions were the same as described in the previous paragraph; after each stripping step the phases were separated and after centrifugation the metal content was analysed in both phases.

The results of all the stripping experiments are represented by the stripping percentage (%*S*), which describes the percentage of a particular metal that is back-extracted from the ionic liquid phase to the aqueous phase. Depending on the metal concentration of the specific metal, either equation (1) or equation (2) was used to calculate the stripping percentage.

$$\%S = \frac{[M]_{aq}}{[M]_0} \qquad (1)$$

$$\%S = \frac{[M]_0 - [M]_{IL}}{[M]_0} \qquad (2)$$

Here $BX - \%. = \left(\frac{[M]_{aq}}{[M]_0}\right) * 100\%$ $[M]_{aq}$ is the concentration of the metal in the aqueous phase after stripping, $[M]_{IL}$ is the concentration of the metal in the ionic liquid after stripping and $[M]_0$ is the initial concentration of the metal in the ionic liquid phase before stripping. Equation (1) was used when the metal element concentration was lower in the aqueous phase than in the ionic liquid phase after stripping. On the other hand, equation (2) was used when the ionic liquid phase contained the lowest metal element concentration. The lowest

concentration was measured, because the absolute errors are much smaller and thus the %*S* value is more accurate.

Results and discussion

Dissolution experiments

For the dissolution of metal oxides in an acid-saturated ionic liquid several preconditions need to be fulfilled. First of all, the ionic liquid has to be able to dissolve a sufficiently large amount of acid to convert the required amount of metal oxides. Secondly, the ionic liquid must form two phases in contact with water to carry out the stripping experiments with an aqueous phase. Thirdly, a low solubility of the ionic liquid in water is required to minimise losses of the organic cations to the aqueous phase in order to make the system viable from both an economic and environmental point of view (Abbott et al., 2011b). Fourthly, the ionic liquid needs to be able to keep the metals dissolved, which can be achieved by using an ionic liquid with coordinating anions. Finally, in order to avoid a complicated extraction system it is favourable to choose the anion of the ionic liquid identical with the conjugated base of the acid. All these requirements are fulfilled by choosing the ionic liquid trihexyl(tetradecyl)phosphonium chloride saturated with a concentrated aqueous hydrochloric acid solution, $P_{66614}Cl$–HCl. Although the ionic liquid shows a very low solubility in water (10–80 ppm, depending on the electrolyte concentration), the ionic liquid is able to absorb up to 0.82 mole fraction of water, which corresponds to 13.5 wt% at room temperature (Freire et al., 2008; Neves et al., 2011; Wellens et al., 2012). The fact that water is soluble in the ionic liquid allows saturating the ionic liquid with concentrated hydrochloric acid (37% HCl). Although dry trihexyl(tetradecyl)phosphonium chloride has a very high viscosity (1200 cP at 30 °C) (Bradaric et al., 2003) saturation of the ionic liquid with water and an increase in temperature cause a large decrease of the viscosity (about 100 cP at 60 °C) and allows an

189 easier handling of the ionic liquid (Wellens et al., 2012).

190 The solubility experiments were carried out by adding the metal oxides NiO, CuO, Fe_2O_3,
191 ZnO, CaO, MnO and CoO with a metal concentration of 1 g L^{-1} for each metal to the
192 trihexyl(tetradecyl)phosphonium chloride – hydrochloric acid mixture under intensive stirring
193 for 2 hours at 60 °C. The metal concentrations after dissolution of NiO, CaO, CoO, MnO,
194 CuO, ZnO and Fe_2O_3 in $P_{66614}Cl$–HCl solution are reported in Table 1. All added metal
195 oxides, except Fe(III) and Ca(II), are quantitatively dissolved in the ionic liquid phase.
196 Iron(III) oxide was not completely dissolved after two hours, and longer stirring times were
197 needed for complete dissolution, which occurred after a period of a week. The low calcium
198 content in the ionic liquid phase can be explained by the fact that the mixture becomes
199 biphasic and finely dispersed aqueous droplets are formed upon dissolution of the metal
200 oxides. These droplets settle at the bottom of the flask and were therefore not included in the
201 analysis. When the dispersed water droplets were analysed, the remaining part of the calcium
202 content was found therein. Except calcium, no other metals were detected in the water
203 droplets. This can be explained because all other metals are present as anionic complexes
204 (*vide infra*), forming ion pairs with the phosphonium cations and staying dissolved in the
205 ionic liquid phase. On the other hand, calcium is not able to form anionic complexes and is
206 present as a hydrated calcium ion, which is easily transferred to the aqueous phase when the
207 mixture starts to become biphasic. The biphasic behaviour can be explained by two effects by
208 which the solution exceeds the saturation limit; firstly the dissolution of metal oxides is
209 producing water as a reaction product and secondly the metal ions present in the solution can
210 induce changes in the physical properties, such as water miscibility. Although relatively low
211 metal concentrations were chosen to prove the dissolution of metal oxides in the acidified
212 ionic liquid, the theoretical amount of metal oxides able to dissolve is determined by the
213 amount of hydrochloric acid present in the ionic liquid solution and corresponds – in the

system described in this paper – to 0.62 M for divalent metal oxides (e.g. for nickel this will be 36 g L^{-1}). However, divalent anionic chlorometallate complexes strongly influence the viscosity of the ionic liquid solution and practically the maximum metal loading limit is about 15–20 gL^{-1} (Wellens et al., 2012). The dissolution of metal oxides in acid saturated ionic liquids offers particular opportunities to bring metal ions in ionic liquid solution, which cannot enter the ionic liquid phase via extraction, such as calcium and nickel. As such it offers opportunities to further process these metals in the ionic liquid phase (Wellens et al., 2012). Furthermore, the dissolution of metal oxides (and in general metals salts) in an ionic liquid is of interest for metal extraction from one ionic liquid to another ionic liquid or to another organic phase (Wellens et al., 2013). The selectivities can be different from those observed for aqueous systems, since the solvation abilities of the metal ion in ionic liquids can be different with respect to an aqueous solution.

[Insert Table 1]

Knowledge of the metal speciation in the ionic liquid solution is of importance for optimisation of the ionometallurgical process. Although the divalent ions Ni(II), Co(II), Cu(II), Mn(II) and Zn(II) and the trivalent Fe(III) occur as tetrachloro complexes in ionic liquids with chloride anions (De Vreese et al., 2012; Estager et al., 2011; Hayashi and Hamaguchi, 2004; Hitchcock et al., 1993; Neve et al., 2001; Pitula and Mudring, 2010), the occurrence of these ions in an acid-saturated ionic liquid solution has to be verified. The absorption spectra of the ionic liquid solutions containing the individual metal ions were recorded after dissolution of their metal oxides (Figure 1). Ni(II), Cu(II), Fe(III), and Co(II) were found to be present as their anionic tetrachlorometallate complexes. In Table 2 the absorption maxima for the different tetrachloro complexes are assigned and the absorption

maxima correspond with literature data. Since the speciation of manganese(II) and zinc(II) could not be determined by optical absorption spectroscopy and since similar behaviour as the other metal species has been described in the literature, their existence as tetrachlorometallate(II) complexes is assumed (Daud and Cattrall, 1982; Miller and Fuersten, 1970; Sato et al., 1984). The presence of calcium as a partly hydrated metal ion can be assumed and could explain why calcium is immediately transferred to the aqueous phase as soon as biphasic behaviour occurs. The dissolution process of the metal oxides in the $P_{66614}Cl$–HCl system are summarised in the following three equations: equation (3) is applicable to the divalent metals where M = Ni(II), Co(II), Zn(II), Cu(II), Mn(II), whereas equation (4) holds for Fe(III) and equation (5) for Ca(II).

$$2P_{66614}Cl + MO + 2HCl \rightarrow [P_{66614}]_2[MCl_4] + H_2O \quad (3)$$

$$2P_{66614}Cl + Fe_2O_3 + 6HCl \rightarrow 2[P_{66614}][FeCl_4] + 3H_2O \quad (4)$$

$$P_{66614}Cl + CaO + 2HCl + xH_2O \rightarrow P_{66614}Cl \cdot CaCl_2.(H_2O)_{x+2} \quad (5)$$

[Insert Figure 1]

[Insert Table 2]

Additionally, the dissolution of metal oxides in the acid saturated ionic liquid was compared with the dissolution in pure HCl solution (12 M HCl) and with the dissolution in the water saturated ionic liquid. It was found that dissolution of the acid-saturated ionic liquid was similar to the dissolution of metal oxides in hydrochloric acid, although for the acid-saturated ionic liquid longer reaction times were necessary because of the higher viscosity and slower mass transfer. On the contrary, the water saturated ionic liquid was not able to dissolve the metal oxides except for calcium oxide. As expected, the dissolution of the metal oxides in the

acid-saturated ionic liquid can be fully ascribed to the reaction with the reactive protons of the added hydrochloric acid.

Stripping experiments

The stripping behaviour of the metal ions present in the trihexyl(tetradecyl)phosphonium chloride – hydrochloric acid solution was investigated as a function of the hydrochloric acid concentration in the aqueous phase. One can argue about the term "stripping" (or back-extraction) instead of extraction since the metal ions were originally present in the ionic liquid solution and are extracted only once because stripping is generally used for the redistribution of a component from an organic phase to an aqueous phase. We will, therefore, use the term "stripping" for describing this experiment. Only aqueous hydrochloric acid solutions were considered because the conjugate base of this acid is the same as the anion of the ionic liquid and mixtures of anions would be undesirable. It was found that nickel and calcium are quantitatively back-extracted to the aqueous phase over the entire HCl concentration range (Figure 2). This can be explained by the strong tendency of nickel(II) and calcium(II) to form aqua complexes. Cobalt(II) and manganese(II) were partly back-extracted only at low HCl concentrations, but zinc(II) and copper(II) and iron(III) could not be removed from the ionic liquid phase. Based on the extraction behavior of the different metal ions, it is possible to separate calcium and nickel from manganese and cobalt and further from zinc, copper and iron. This system can be of special interest for the recovery of nickel from a mixture of metals, since nickel can be removed in one step from all other transition metals present in the solution. Nevertheless, the mutual separation of calcium from nickel, of cobalt from manganese, and of copper from zinc and iron with this ionic liquid system is impractical, because of the poor selectively of these separations.

[Insert Figure 2]

294

295

296 **Recovery the ionic liquid phase: removal of copper, zinc and iron**

297 In order to reuse the ionic liquid, iron, copper and zinc have to be removed. For the removal
298 of iron from trihexyl(tetradecyl)phosphonium chloride, stripping with EDTA was proposed
299 (Vander Hoogerstraete et al., 2013). Copper(II) and zinc(II) can be removed simultaneously
300 with iron(III) by stripping with EDTA. However, since EDTA is too expensive for application
301 in industrial hydrometallurgical processes, ammonia was tested as a stripping agent. In
302 ammonia solutions, copper will form the complex $[Cu(NH_3)_4]^{2+}$ and zinc(II) the complex
303 $[Zn(NH_3)_4]^{2+}$ which have a much higher stability constant ($\beta = 10^{12}$ and 10^9, respectively)
304 (Holleman et al., 2001; Sharma R.K., 2007) compared to the anionic chloro complexes
305 $[CuCl_4]^{2-}$ and $[ZnCl_4]^{2-}$ at low chloride concentrations ($\beta = 1$ and 10^1, respectively) and these
306 complexes are easily transferred to the aqueous phase (Bjerrum and Skibsted, 1977; Morris
307 and Short, 1962; Ohlson and Vannerberg, 1974; Short and Morris, 1961).

308 In these alkaline conditions iron will precipitate as iron(III) hydroxide. In a continuous
309 process, the three phases (i.e. the recovered ionic liquid phase, the aqueous solution with
310 copper(II) and zinc(II) and the iron(III) hydroxide precipitate) can be separated in one step by
311 using a solid bowl centrifuge (Merkl and Steiger, 2012). Figure 3 shows that after treatment
312 the ionic liquid solution with an aqueous ammonia solution, copper(II) is stripped to the
313 aqueous phase (right) and that iron(III) is precipitated, this precipitate is collected at the
314 interface after centrifugation (left). After phase separation by centrifugation, no measurable
315 metal content was found in the ionic liquid phase. In order to generate the ionic liquid phase
316 for reuse, a pretreatment step consisting of washing the ionic liquid with an aqueous
317 hydrochloric acid solution must be included.

318

[Insert Figure 3]

^{31}P NMR spectra

Although it was reported that tetraalkylphosphonium halides can be combined with concentrated sodium hydroxide without any degradation (Fraser and MacFarlane, 2009; Wolff et al., 2000; Zanger et al., 1959). Examples are reported where tetraalkylphosphonium salts dissolved in organic solvents are not always stable in the presence of hydroxides or other bases, forming a tertiary alkylphosphine oxide and an alkane.(Fraser and MacFarlane, 2009; Zanger et al., 1959) Therefore, the stability of trihexyl(tetradecyl)phosphonium chloride ionic liquid was investigated by analysis of the degradation products formed after mixing the ionic liquid phase with an aqueous ammonia solution. This was done by recording the ^{31}P NMR spectrum of the ionic liquid and by integrating the resonance signal of phosphine oxide situated at 49.6 ppm and comparing it to the resonance signal of the trihexyl(tetradecyl)phosphonium cation at 32.7 ppm. The ^{31}P NMR spectra were measured for the ionic liquid free of dissolved metals, in order to avoid paramagnetic impurities. The peak integration ratios were then compared with the ^{31}P NMR spectra of trihexyl(tetradecyl)phosphonium chloride as it was received. It was found that the commercial trihexyl(tetradecyl)phosphonium chloride (Cyphos® IL 101) as received from the supplier already contained a small phosphine oxide content but no increase in the amount phosphine oxide was found on treatment with ammonia. This means that the washing step with ammonia is justified as a process step, since no additional degradation of the ionic liquid was observed.

Multistep stripping

In order to remove the metals from the ionic liquids, a multistep stripping procedure was applied on the ionic liquid-acid solution. The first stripping stage made use of a 6 M HCl

aqueous solution. Thereafter, the ionic liquid solution was washed three times with water. Finally, the ammonia stripping procedure just described was performed to recycle the ionic liquid for reuse. It was found that after the first acid extraction step, nickel and calcium were stripped with an efficiency of 99.1% and 98.3%, respectively (Table 3). However, impurities of manganese and cobalt were co-extracted to the aqueous phase (3.8% and 0.5%, respectively). After two washing stages with water, manganese (99%), cobalt (92.2%) and iron (35%) were removed from the ionic liquid phase. The distribution for cobalt, manganese and iron is strongly dependent on the hydrochloric acid concentration (Vander Hoogerstraete et al., 2013). In order to remove the remaining cobalt (7.7%) and manganese (1%) from the ionic liquid phase, a third washing step was necessary. However, copper (14.6%) started to transfer to the aqueous phase at this stage. These facts highlight the difficult mutual separation of all transition metals except for nickel. Given the fact that nickel is separated from all other transition elements, this system is especially interesting for applications in which nickel needs to be removed from other transition metal impurities such as iron, cobalt, manganese, cobalt or zinc. Finally, iron, copper and zinc are removed from the ionic liquid phase applying the stripping with ammonia. This leads to a metal-free ionic liquid that can be used for a new dissolution step of metal oxides. The schematic representation of the dissolution and subsequent stripping of the metal ions in the acid-saturated ionic liquid is shown in Figure 4.

[Insert Table 3]

[Insert Figure 4]

Conclusions

The use of an acid-saturated ionic liquid system has been used to overcome the problem of low metal solubility in ionic liquids and allows further processing of the metal ions from the

ionic liquid phase. Trihexyl(tetradecyl)phosphonium chloride (Cyphos® IL 101) saturated with hydrochloric acid was found to dissolve large amounts of the metal oxides, to be insoluble in the aqueous phase and to be stable to mildly basic aqueous ammonia solutions. The stripping of the dissolved metals from the ionic liquid to the aqueous phase was demonstrated; nickel and calcium were separated from cobalt, manganese, and copper, zinc and iron. The mutual separation between cobalt, manganese, copper and iron is difficult. Recovery of the ionic liquid was possible by changing the stripping conditions and the ionic liquids could be reused after removal of iron, zinc and copper by washing with an ammonia solution. This process is of particular interest for the separation of nickel from other transition metal ions, because nickel can be removed in one step from cobalt, manganese, iron, copper and zinc.

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Table 1: Measured metal content of the $P_{66614}Cl$-HCl solution after dissolution of the oxides.[a]

Metal oxide	Metal content (mg L^{-1})
NiO	996 (±2)
CaO	698 (±36)
CoO	993 (±10)
MnO	994 (±27)
CuO	1035 (±8)
ZnO	1041 (±10)
Fe_2O_3	647 (±11)

[a] To the acid-saturated ionic liquid, an amount of metal oxide was added, which would result after complete dissolution to a concentration of 1000 mgL^{-1}.

Table 2: Assignment of the absorption maxima typical for the tetrachlorometallate complexes present in the absorption spectra shown in Figure 1.

$[MCl_4]^{x-}$	λ_{max} (nm)	Transition	References
$[NiCl_4]^{2-}$	236, 261, 284 660, 708	LMCT[a] ($Cl^- \rightarrow Ni^{2+}$) *d-d:* $^3T_1(P) \leftarrow {}^3T_1$	(Goodgame et al., 1961; Lever, 1968)
$[CoCl_4]^{2-}$	236 697, 670,636	LMCT ($Cl^- \rightarrow Co^{2+}$) *d-d:* $^4T_{1g}(P) \leftarrow {}^4A_2$	(Cotton et al., 1961; Lever, 1968; Orgel, 1955; Wellens et al., 2012)
$[CuCl_4]^{2-}$	414, 296, 245	LMCT ($Cl^- \rightarrow Cu^{2+}$)	(De Vreese et al., 2012; Lever, 1968; Sharnoff and Reimann, 1967)
$[FeCl_4]^-$	243, 316, 247	LMCT ($Cl^- \rightarrow Fe^{3+}$)	(Jorgensen, 1962; Lever, 1968)

[a] LMCT = ligand-to-metal charge transfer

Table 3: Cumulative stripping percentage (%*S*) after each stripping step.

Stripping step	Stripping agent	Ni (%)	Ca (%)	Co (%)	Mn (%)	Cu (%)	Zn (%)	Fe (%)
1	6 M HCl	99.1	98.3	0.5	3.8	0.1	0.0	0.1
2	water	100	100	27.6	61.7	0.0	0.0	4.4
3	water	0.0	0.0	92.3	99	0.0	0.0	35
4	water	0.0	0.0	100	100	14.2	0.0	66.6
5	NH_3 (5 wt%)	0.0	0.0	0.0	0.0	100	100	100

401

Figure Captions

403

Figure 1. Absorption spectra of the individual tetrachlorometallate complexes after dissolution of their metal oxides in the $P_{66614}Cl$–HCl mixture (metal content is 5 gL^{-1}).

406

Figure 2: Stripping percentage (%*S*) of the different metal ions as a function of the HCl concentration in the aqueous phase.

Figure 3: Left: iron(III) hydroxide precipitate, formed upon treatment of the ionic liquid phase with an aqueous ammonia solution. Right: stripping of copper(II) from the ionic liquid phase by an aqueous ammonia solution.

Figure 4: Flow chart for the dissolution of metal oxides and the separation of the dissolved metals by stripping to the aqueous phase. The ionic liquid stream is shown in black, the aqueous steams in blue and the metal oxides or metal hydroxides in red.

415

Figure 1

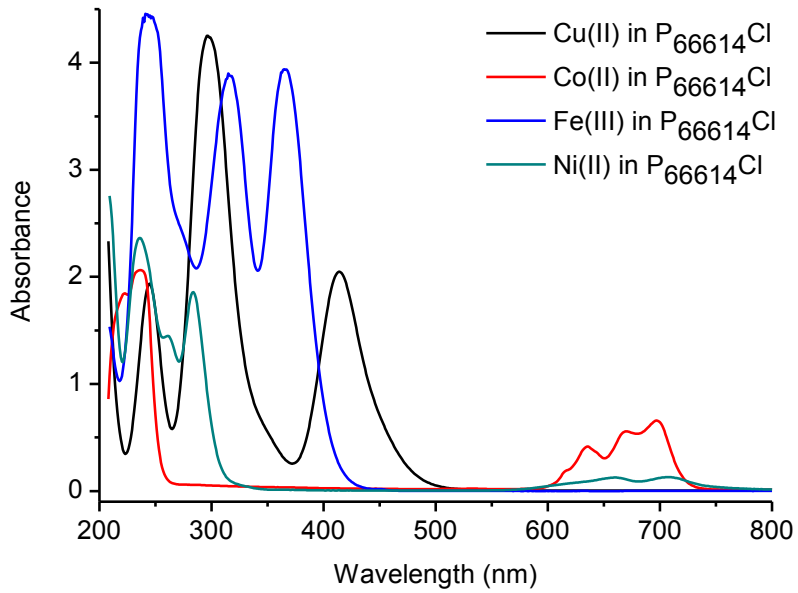

Cu(II) in $P_{66614}Cl$
Co(II) in $P_{66614}Cl$
Fe(III) in $P_{66614}Cl$
Ni(II) in $P_{66614}Cl$
Absorbance
Wavelength (nm)
0
1
2
3
4
200
300
400
500
600
700
800

Figure 2

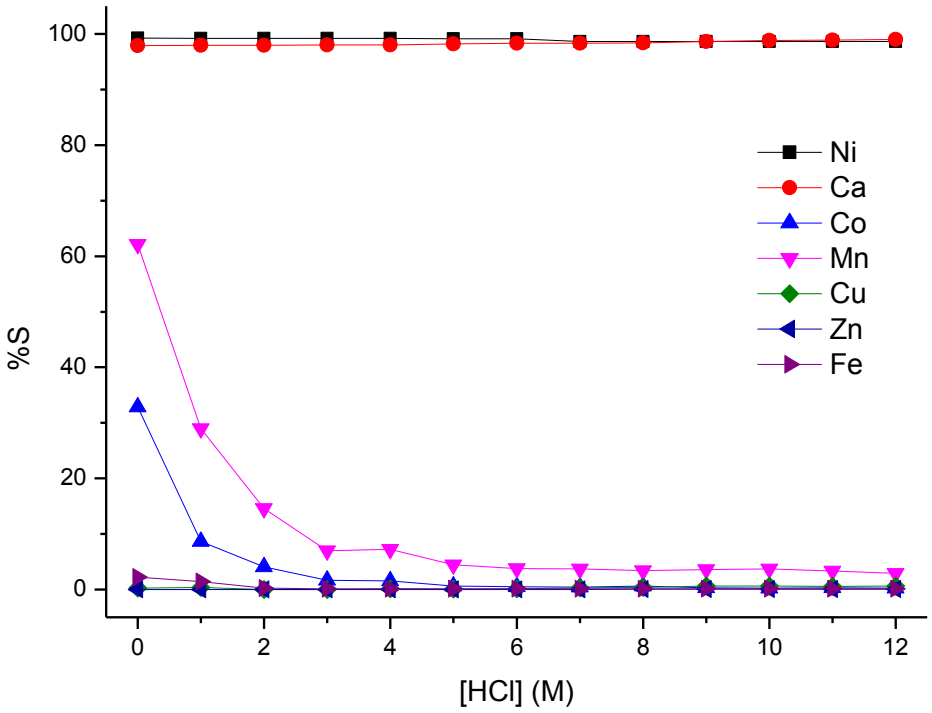


Figure 3

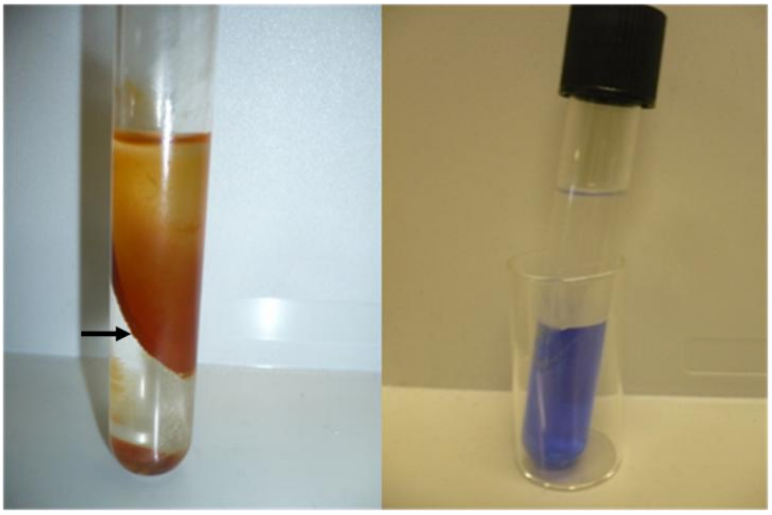
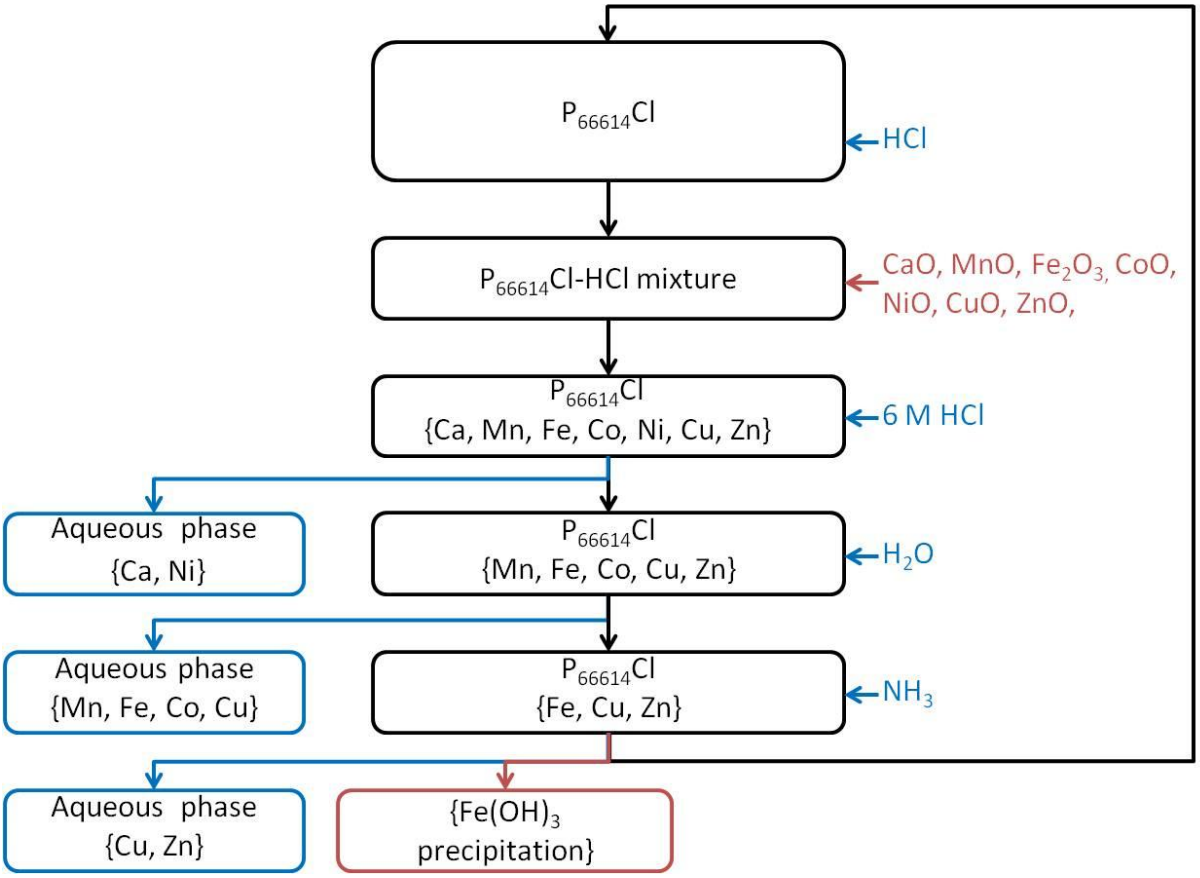


Figure 4


P66614Cl
HCl
P66614Cl-HCl mixture
CaO, MnO, Fe2O3, CoO, NiO, CuO, ZnO,
P66614Cl {Ca, Mn, Fe, Co, Ni, Cu, Zn}
6 M HCl
Aqueous phase {Ca, Ni}
P66614Cl {Mn, Fe, Co, Cu, Zn}
H2O
Aqueous phase {Mn, Fe, Co, Cu}
P66614Cl {Fe, Cu, Zn}
NH3
Aqueous phase {Cu, Zn}
{Fe(OH)3 precipitation}

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